

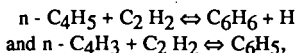
THE FORMATION OF BENZENE IN FLAMES

James A. Miller and Carl F. Melius
Sandia National Laboratories
Livermore, CA 94551-0969

Introduction

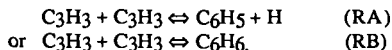
The mechanism by which aromatic compounds are formed in flames of aliphatic fuels is currently a "hot topic" in combustion. This interest stems from the importance of small aromatic compounds in the formation of PAH (polycyclic aromatic hydrocarbons) and soot (undesirable by-products) in combustion processes. The formation of the "first ring" is a key step in such processes and may well be rate limiting. The identification of the elementary reactions leading to the first aromatic compound consequently is of paramount importance.

Perhaps the two most cited reactions leading to cyclization (i.e., ring formation) are the reactions,



where C_6H_6 is benzene and C_6H_5 is phenyl. Unfortunately, both $n\text{-C}_4\text{H}_3$ and $n\text{-C}_4\text{H}_5$ have isomers, $i\text{-C}_4\text{H}_3$ and $i\text{-C}_4\text{H}_5$, that are more stable than they are, and distinguishing between the isomers on a mass spectrometer (the diagnostic tool in most flame experiments) is impossible. Consequently, to determine the extent to which these reactions occur in a flame requires a thorough understanding of the "pre-cyclization" chemistry. In fact, a thorough understanding of the pre-cyclization chemistry is essential in determining what the cyclization steps are in any event.

In the present paper, we review the mechanism we have proposed previously^(1,2) for the formation of C_3 and C_4 hydrocarbons in rich acetylene flames. In doing this we compare the predictions of our kinetic model with the experimental results of Bastin, et al.⁽³⁾ and Westmoreland,⁽⁴⁾ in lightly sooting $\text{C}_2\text{H}_2/\text{O}_2/\text{Ar}$ flames. In addition, we discuss the implausibility of reactions (R191) and (R190) (reaction numbers refer to the table in Ref. 1) as primary cyclization steps in such flames. We show that the reaction between two propargyl radicals,



is a much better candidate for forming the first ring. This leads us to perform extensive BAC-MP4 calculations on this reaction and to interpret the extensive amount of low-temperature pyrolysis data on non-aromatic C_6H_6 compounds in terms of this potential.

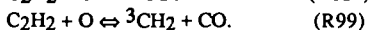
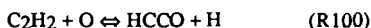
FLAME CALCULATIONS, CHEMICAL KINETICS, AND THERMODYNAMICS

The flame calculations discussed in this paper were performed in the same manner as described previously,^(1,2) using the Sandia flame code.^(5,6) Thermodynamic data come primarily from the Chemkin thermodynamic data base,⁽⁷⁾ supplemented by BAC-MP4 results for some key

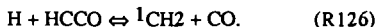
C₃ and C₄ species. These species have subsequently been added to the Chemkin data base. The reaction mechanism is the same as that described in Refs. 1 and 2. This mechanism utilizes the rate coefficient expressions given by Westmoreland for reactions (R190) and (R191).

THE FORMATION OF C₃ AND C₄ HYDROCARBONS

Even in sooting acetylene flames the dominant C₂H₂ removal step is the two - channel reaction,



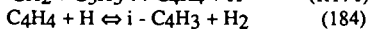
In rich flames, the ketyl formed in reaction (R100) reacts primarily with hydrogen atoms to form ¹CH₂,



The presence of ¹CH₂ in these flames has important consequences for the formation mechanism of C₃ and C₄ hydrocarbons.

Singlet methylene, ¹CH₂, inserts rapidly into acetylene, forming propargyl and a hydrogen atom,
$${}^1\text{CH}_2 + \text{C}_2\text{H}_2 \rightleftharpoons \text{C}_3\text{H}_3 + \text{H}. \quad (\text{R143})$$

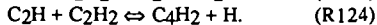
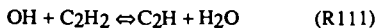
Reaction (R143) is the primary source of propargyl, which is principally consumed by reaction with H-atoms. Vinyl acetylene (C₄H₄) and C₄H₃ are formed by the reactions.



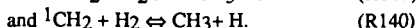
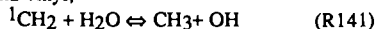
Diacetylene, C₄H₂, comes from



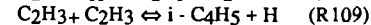
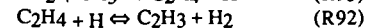
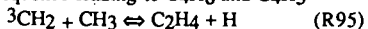
as well as the sequence



Butadiene and the butadienyl radical, C₄H₆ and C₄H₅, are formed from ¹CH₂ by circuitous routes through ethylene and vinyl,



Reactions (R140) and (R141) are the most important sources of methyl in these flames. There then follows the reaction sequence leading to C₄H₆ and C₄H₅



Figures 1 and 2 show comparisons of our model predictions with the experiments of Westmoreland for C₃H₃ and with those of Bastin et al. for C₄H₃ and C₄H₅. Many other comparisons are shown in Refs. 1 and 2.

FORMATION OF BENZENE

In the reaction mechanism of Ref. 1, there are only two ways to form benzene,



followed by phenyl either adding or abstracting a hydrogen atom, and

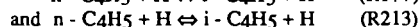


Because of the low levels of both isomers of C₄H₅ in the flame, neither (R190) nor its i-C₄H₅ counterpart is ever an effective route to benzene formation in our model. Consequently, all the benzene formed is through phenyl. In competition for phenyl with reactions that produce benzene are the oxidative paths.



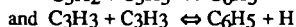
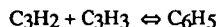
In order to be conservative about eliminating reactions as possible sources for benzene, we have in some cases added the C₆H₆ and C₆H₅O predictions to compare with the experimental benzene profiles

Figure 3 shows comparisons of model predictions with the experimental results for benzene from Bastin, et al.⁽³⁾. The basic model is unable to predict the benzene concentrations measured in the flame primarily because of the reactions,



which render the n-isomers very small fractions the total radical concentrations in the flame. Even increasing k₁₉₈ and k₁₉₇ by a factor of ten (an unreasonable increase) does not result in sufficient benzene levels. Neither does including reactions of i-C₄H₃ and i-C₄H₅ with acetylene to form benzene. The fact that case (d) in Fig. 3 comes close to the experiment really implies that all the C₄H₃ would have to be the i-isomer to predict the benzene levels observed.

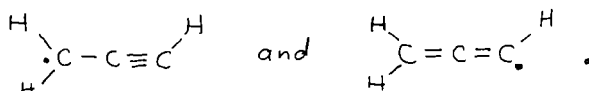
From Fig. 3 one can see that only the reactions,





are capable of predicting the benzene levels observed in the flame. The first of these reactions, because of the high rate coefficient required and because our model overpredicts the C₃H₂ concentrations observed by Westmoreland (thus implying an even higher rate coefficient), is a less attractive candidate than the second. The second reaction, the recombination of two propargyl radicals, has been suggested as a source of benzene in shock tube experiments on the pyrolysis of allene and propyne by Kern and co-workers^(8,9) and, independently and concurrently with our work, ⁽¹⁾ has been suggested by Stein, et al. ⁽¹⁰⁾ as a possible source of benzene in acetylene flames.

PROPARGYL RADICAL RECOMBINATION

In order to test the viability of forming an aromatic compound, i.e., either $C_6H_5 + H$ or C_6H_6 , from the recombination of two propargyl radicals, we have performed an extensive set of BAC-MP4 electronic structure calculations. The results are presented in Figs. 4 and 5. Propargyl is a resonantly stabilized radical with the two structures,



If we refer to the end of the radical with two hydrogens as the head and the end with one hydrogen as the tail, Fig. 4 shows the intermediate structures and potential energy barriers encountered in head-to-head or tail-to-tail recombination, and Fig. 5 shows those encountered in head-to-tail recombination.

Our potential is at least qualitatively consistent with a variety of low-temperature pyrolysis experiments⁽¹⁰⁾ which show 3,4 - dimethylenecyclobutene  and fulvene  as primary products of both 1,5 - hexadiyne ($\equiv - - - \equiv$) pyrolysis and 1,2,4,5 - hexatetraene ($= - - =$) pyrolysis. Our one inconsistency with these experiments is the implication that there is a low energy path to benzene from 1,5 hexadiyne and 1,2,4,5 hexatetraene. We have not yet found one. The implication of these results we discussed in Ref. 1. However, we do find an energetically accessible path from $C_3H_3 + C_3H_3$ to benzene and to phenyl + H via head-to-tail recombination, as shown in Fig. 5. Thus, our calculations confirm the possibility of forming benzene in flames by a relatively fast reaction between two propargyl radicals. Such a result is also consistent with the experiments of Alkemade and Homann⁽¹¹⁾, which show a fast $C_3H_3 + C_3H_3$ rate coefficient and show benzene as a major product.

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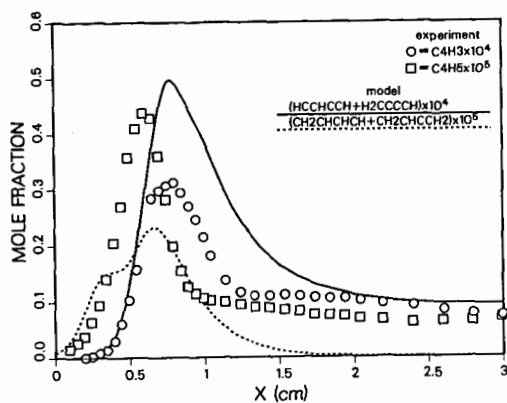


Figure 1. Comparison of model predictions with the experiments of Bastin, et al. for C₄H₃ and C₄H₅.

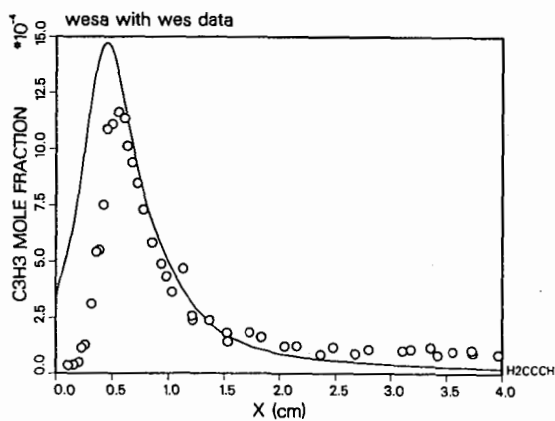


Figure 2. Comparison of model predictions with the experiments of Westmoreland for C₃H₃.

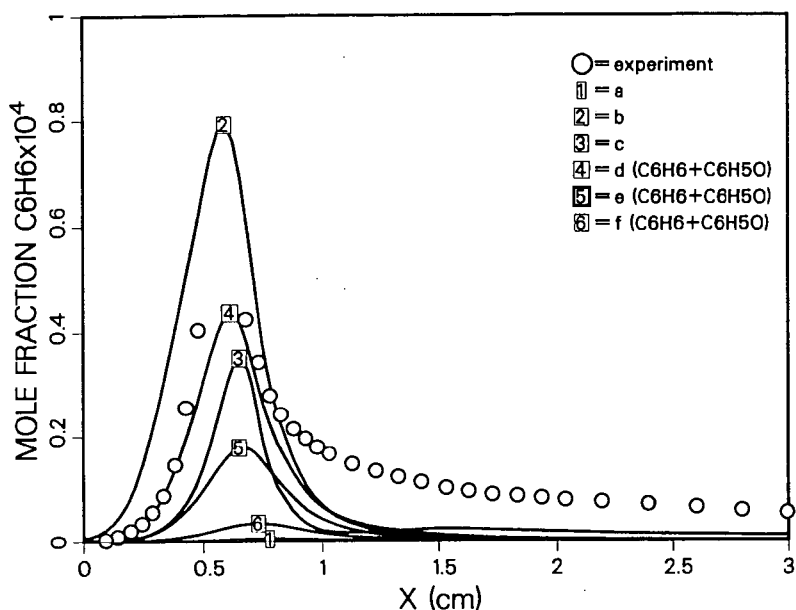


Figure 3 Comparison of model predictions with the experiments of Bastin, et al. for benzene (a) model of Ref. 1, (b) model of Ref. 1 with the addition of $\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 \rightleftharpoons \text{C}_6\text{H}_5 + \text{H}$ ($k = 1 \times 10^{13} \text{cm}^3/\text{mole-sec}$); (c) model of Ref. 1 with the addition of $\text{C}_3\text{H}_3 + \text{C}_3\text{H}_2 \rightleftharpoons \text{C}_6\text{H}_5$ ($k = 5 \times 10^{13} \text{cm}^3/\text{mole-sec}$.); (d) model of Ref. 1 with the addition of $i\text{-C}_4\text{H}_3 + \text{C}_2\text{H}_2 \rightleftharpoons \text{C}_6\text{H}_5$ and $i\text{-C}_4\text{H}_5 + \text{C}_2\text{H}_2 \rightleftharpoons \text{C}_6\text{H}_6 + \text{H}$ (same rate coefficients as for the analogous $n\text{-C}_4\text{H}_3$ and $n\text{-C}_4\text{H}_5$ reactions); (e) model of Ref. 1 with k_{190} and k_{191} increased by a factor of ten; (f) model of Ref. 1 with the heat of formation of $i\text{-C}_4\text{H}_3$ increased to 121.7 kcal/mole. In cases d, e, and f, the predictions are for the sum of C_6H_6 and $\text{C}_6\text{H}_5\text{O}$

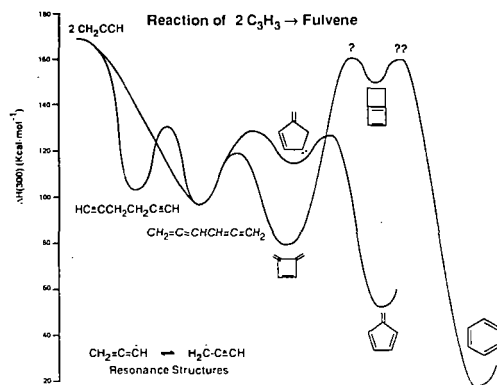


Figure 4. Potential energy diagram for head-to-head or tail-to-tail recombination of two propargyl radicals.

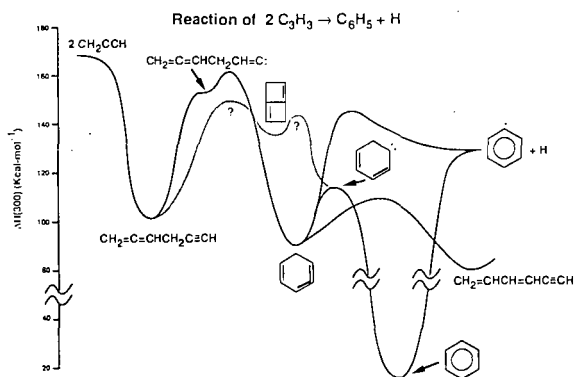


Figure 5. Potential energy diagram for head-to-tail recombination of two propargyl radicals.